

Localization phenomena in models of ion-conducting glass formers

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Abstract. The mass transport in soft-sphere mixtures of small and big particles as well as in the disordered Lorentz gas (LG) model is studied using molecular dynamics (MD) computer simulations. The soft-sphere mixture shows anomalous small-particle diffusion signifying a localization transition separate from the big-particle glass transition. Switching off small-particle excluded volume constraints slows down the small-particle dynamics, as indicated by incoherent intermediate scattering functions. A comparison of logarithmic time derivatives of the mean-squared displacements reveals qualitative similarities between the localization transition in the soft-sphere mixture and its counterpart in the LG. Nevertheless, qualitative differences emphasize the need for further research elucidating the connection between both models.

1 Introduction

Transport in heterogeneous disordered materials and in porous media arises in many diverse subjects of science and engineering such as water resource management, oil recovery, the physics of crowded biological systems, glass technology or even the geophysical understanding of the eruption of volcanos [1]. Examples are fast ion transport in alkali-silicate melts and other industrially relevant glass formers [2], protein motion on cell membranes [3,4] and within the living cell [5], among others. Common to all these materials is that they consist of at least two components, one of which (the “fast

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component”) is responsible for the observed transport phenomena, while the other forms the heterogeneous matrix and is either completely frozen as, e.g., in porous media, or relaxes orders of magnitude slower, as in glass-forming ion conductors.

A well-known reference point for diffusion in random environments is the Lorentz gas (LG) [6, 7]: considering a single particle diffusing through a set of fixed obstacles, one essentially arrives at an off-lattice model for the transport through porous media or ion-conducting systems. The LG exhibits a localization transition where diffusion of the tracer ceases altogether if the density of scatterers exceeds a certain value; this transition is understood as a dynamic critical phenomenon connected with the percolation of void space in the heterogeneous background medium [8, 9].

Obviously, several aspects of ion-conducting systems are described in an oversimplified manner by the LG model. In a real ion conductor, the frozen environment is not formed by fixed obstacles that are randomly distributed. Instead, the “obstacle particles” exhibit structural correlations (at least on short length scales) and they are subject to thermal motion. Moreover, in most ion-conducting systems the mobile ions cannot be considered as non-interacting tracer particles and the correlations between ions have to be taken into account. Realistic modeling for sodium silica melts [10–12] reveals that the silica network can constitute such a quasi-arrested array of correlated obstacles through which sodium ions meander on preferential diffusion pathways. The chemical properties of the silica melt to form a tetrahedral network appears not to be essential: a similar decoupling of diffusive transport is observed in dense size-asymmetric Yukawa melts [13] and binary soft-sphere mixtures [14, 15]. Mode-coupling theory has been used to predict it for size-disparate hard-sphere systems [16, 17]. As shown recently by molecular dynamics (MD) computer simulations [18], such systems may exhibit a glass transition where the fast component remains mobile even for high-density states at which the matrix does not show relaxation over the entire simulation time window. At these high densities, evidence was found that the small particles show anomalous diffusion and approach a localization transition that bears resemblance to the LG transition. Similar findings hold for an entirely frozen matrix, where non-trivial predictions of a mode-coupling theory developed by Krakoviack [19–21] have been tested recently [22, 23]. However, it is an open question to what extent the small-particle localization dynamics in binary soft-sphere mixtures can be understood as a dynamic critical phenomenon that falls into the same universality class as the localization transition of the LG [8, 9] and other continuum percolation models [24]. In particular, the question arises how the localization of the small particles is affected by interactions between the mobile tracers.

In this contribution, we present first steps to address the latter issues. We compare on a qualitative level the anomalous diffusion of a binary soft-sphere mixture with that of a LG. The effect of collective interactions among the small particles is investigated by switching off their interactions.

2 Results

We performed MD simulations of an equimolar binary mixture of purely repulsive soft spheres (BSSM) with a size ratio of 0.35. Diameters are chosen additively, and nonadditive energetic interactions further decouple the species. Temperature is unity, and all masses are equal. For details, see Ref. [18]. MD simulations of the LG were carried out using an event-driven algorithm and randomly distributed, possibly overlapping hard sphere obstacles. The dimensionless obstacle density n^* is the only control parameter of the model; details can be found in Ref. [9].

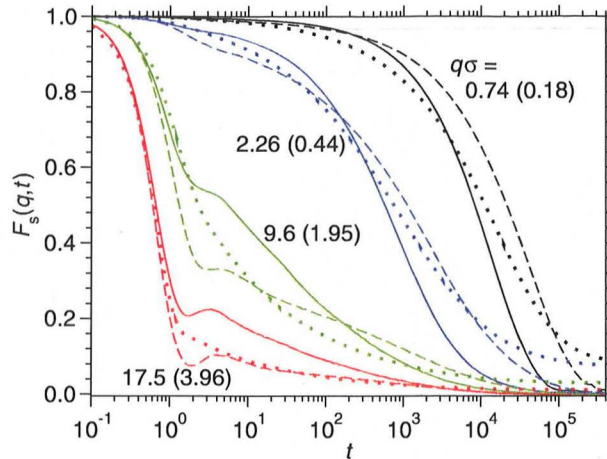


Fig. 1. Incoherent intermediate scattering function $F_s(q, t)$ for the small/tracer particles. Solid and dashed lines correspond respectively to the BSSM with and without interactions among the small particles, while dotted lines represent the LG model. For the BSSM, the wavenumbers are in the range $0.74 \leq q\sigma \leq 17.5$, as indicated (with σ the diameter of the big particles). The wavenumbers in brackets correspond to the LG. The number density of the BSSM is $\rho = 3.26$. For the LG, the packing fraction of the obstacles is $n^* = 0.75$.

Figure 1 shows the time dependence of the incoherent intermediate scattering function, $F_s(q, t)$, of the small particles for different values of the wavenumber q , as indicated. For the BSSM, at a number density $\rho = 3.26$, the big particles form a glass and the transport of the small particles is characterized by anomalous subdiffusive motion crossing over to ordinary diffusion at long times. Two kinds of BSSM systems are considered in Fig. 1: the solid lines correspond to the system with interacting small particles, while the dashed lines correspond to a system where the small-small interaction potential is set to zero, keeping all other parameters fixed. Structure and dynamics of the big particles as measured through the partial static structure factor are unaffected by this [18]. Surprisingly, at fixed q the curves for the fully interacting case decay more rapidly than those for the non-interacting case. In Ref. [18], we have proposed that this difference arises because small-particle interactions result in a more directional and thus more effective diffusive motion.

Also shown in Fig. 1 are results for the LG at a packing fraction of the obstacles $n^* = 0.75$. At this value of n^* , the decay of $F_s(q, t)$ takes place on a similar time scale provided that one reduces the wavenumbers by about a factor of 4 (as done in Fig. 1) to match the length scales of the LG and the BSSM systems. The curves for the LG demonstrate the absence of a “glassy” plateau at intermediate times. At long times, they decay to a plateau of different origin: the presence of closed, finite pockets in the obstacle matrix leads to a localization of tracer particles. However, apart from that the decay of the LG correlators is similar to that for the BSSM systems. So the question arises whether the transport as seen for the non-interacting particles in the binary mixture is similar to that seen in the LG.

To address this question, we compare the logarithmic derivative $\gamma(t) = d[\log \delta r^2(t)]/d(\log t)$ for the two binary mixtures and for the LG in Fig. 2; $\gamma(t)$ is calculated from the mean-squared displacements $\delta r^2(t)$ of the mobile particles in both systems. The quantity $\gamma(t)$ has the meaning of an effective exponent that crosses over from $\gamma(0) = 2$ (ballistic short-time motion) to $\gamma(\infty) = 1$ for diffusive particles in the liquid. For localized particles, $\gamma(\infty) = 0$ is expected.

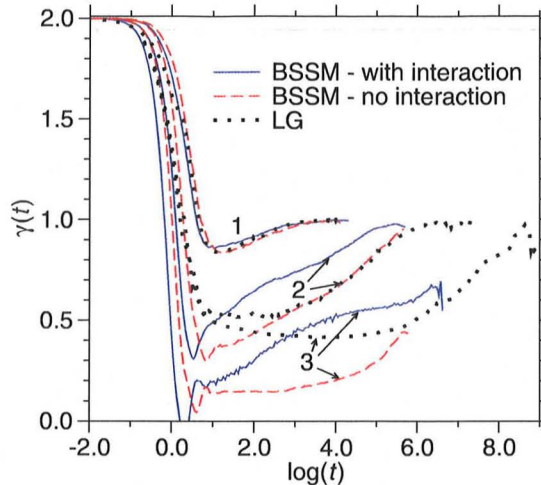


Fig. 2. Effective exponent, as obtained from the logarithmic derivative $\gamma(t)$ of the mobile particles for the binary mixture with and without interactions between the small particles as well as for the LG. Results are shown for different densities: the three sets marked with number 1 correspond to $\rho = 2.296$ and $n^* = 0.40$, those with number 2 to $\rho = 3.257$ and $n^* = 0.75$ and those with number 3 to $\rho = 4.215$ and $n^* = 0.82$ (here, ρ and n^* are the densities of the binary mixtures and the LG, respectively).

The selected obstacle densities for the LG in Fig. 2, $n^* = 0.40, 0.75$ and 0.82 , are below the critical density of the localization transition, $n_c^* = 0.837$ [9]. At criticality $n^* = n_c^*$, the exponent $\gamma(t) \approx 0.32$ is approached at long times [8], thus confirming the universal subdiffusive behavior expected from renormalization group arguments (refer to Ref. [9] for a detailed discussion). Below n_c^* , such anomalous diffusion is seen in a finite, intermediate time window and universal corrections to scaling [25] lead to the observation of an effective exponent that is larger than the universal critical exponent. At $n^* = 0.82$ for example, an effective exponent $\gamma \approx 0.4$ is observed over about four orders of magnitude in time, see Fig. 2.

At low densities (set of curves “1” in Fig. 2), the binary mixtures with and without interactions between the small particles show almost identical behavior as the LG with respect to $\gamma(t)$. Nevertheless, there are quantitative differences: At higher densities the effective exponent of the BSSM without interaction becomes rather small, the corresponding mean-square displacement remains of the order of the interparticle distance, and the cage effect interferes strongly with the regime of anomalous diffusion. Turning on the interaction, a window of subdiffusion emerges, yet the effective exponent drifts gradually from 0.5 to 0.6. In contrast, the LG displays clear subdiffusive behavior over several orders of magnitude in time as manifested in an almost constant $\gamma(t)$, as mentioned above.

Clearly, a simplistic mapping between the BSSM and the overlapping LG is not obvious and may not exist due to the highly simplified character of the LG. Thus, the investigation of LG variants with increasing complexity is desirable, which close the gap to the BSSM. For example, a better approximation of the matrix structure would be obtained by introducing correlated obstacles in the LG (“non-overlapping LG”). Another issue is raised by the hard interaction potentials in the LG. While a tracer with constant velocity between soft obstacles is easily mapped to the hard sphere model, the percolation transition is already smeared out for thermal tracers (or tracers in contact with a heat bath) due to the average over the Maxwell distribution. All these issues are the subject of forthcoming studies.

This collaborative work has been started as part of the Research Unit FOR 1394 of Deutsche Forschungsgemeinschaft (DFG). We acknowledge a substantial grant of computer time at the NIC Jülich. Th. V. acknowledges funding from the Helmholtz-Gemeinschaft (VH-NG 406) and the Zukunftskolleg Konstanz.

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